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GLASS CERAMICS BASED ON SPODUMENE GLASS PRODUCED IN A SOLAR FURNACE

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The effect of the methods for introducing catalysts on phase formation in glass ceramics produced by the ceramic technology from spodumene glass melted in a solar furnace is studied. The main properties of class ceramics are identified. It is indicated that when a catalyst is introduced, the optimum phase composition determining the properties of glass ceramics is formed at lower sintering temperatures. It is established that the methods of ceramic technology can yield glass ceramics with good dielectric characteristics.

Glass ceramic materials, along with traditional ceramics, are extensively used to produce electric engineering parts. The best known and common method for their production is the traditional glass technology. Special attention has been paid lately to the ceramic technology of producing glass ceramic products, which makes it possible to correct their composition and control the properties of the materials. It is known [1, 2] that sintered glass ceramics can be produced by two methods: sintering glass powders of grain size around 10 μm with a catalyst powder additive or sintering glass powders that already contain a catalyst introduced in melting.

We have investigated the effect of the method of introducing catalysts on the properties of glass ceramic materials based on glass of the spodumene composition.

To achieve catalyzed crystallization, we used different catalysts, both metal and oxide ones, as modifiers. The catalysts were introduced by one of two methods. In the first case (method 1) involving a large solar furnace (city of Parkent), spodumene glass was initially synthesized. The initial components were lithium carbonate, aluminum oxide, and mineral material used as a source of SiO_2 and partly of Al_2O_3. The latter material was either quartz sand, or a quartz-kaolinite-pyrophylite rock from the Boinaksaiskoe deposit in Uzbekistan. The respective content of the components for the case with quartz sand was 17.49, 23.39, and 59.12% (here and elsewhere wt.%) and in the case of the quartz-kaolinite-pyrophyllite rock: 17.36, 8.90, and 73.74%, respectively. The melt was poured into water producing granules that were milled in a planetary mill to a grain size of 1 – 2 μm. The cooling rate of the melt was 10^3 K/sec. The x-ray phase analysis of the granules indicated that the synthesized material was amorphous with traces of solid solutions of the quartz-O type.

The finely dispersed powder and the catalyst were mixed in a certain ratio. For complete homogenization of the mixtures, mixing was performed by the wet method in a planetary mill for 2 h with subsequent drying at a temperature of 100 – 110°C. The following additives were introduced into mixtures based on spodumene glass (above 100%), %: Si-6) 1 Si; Si-7) 12 TiO_2; Si-8) 10 TiO_2 and 2 ZrO_2, Si-9) 11 TiO_2 and 1 B_2O_3.

To perform further experiments, articles of different shapes were molded by semidry molding meeting the requirements of GOST 20409–80. The unit molding pressure was 70 MPa.

The second variant (method 2) implies the introduction of modifying components at the moment of batch preparation for the synthesis of spodumene glass with subsequent joint melting and curing. The melt was cooled by pouring it in water (similarly to the method described above).

Heat treatment was performed according to the following schedule: 600°C for 3 h, 700°C for 1 h, at the maximum temperatures of 1050, 1100, 1200, and 1300°C for 1 h. The x-ray phase analysis of crystallized glasses revealed the following. After annealing at 1100°C, the main phase in all phases was β-spodumene; SiO_2 and Al_2O_3 were present as well. The samples with a TiO_2 catalyst additive exhibited the formation of rutile. As the temperature increases to 1200°C, mullite starts to be identified on the diffraction patterns and its quantity grows insignificantly as the temperature grows to 1300°C.

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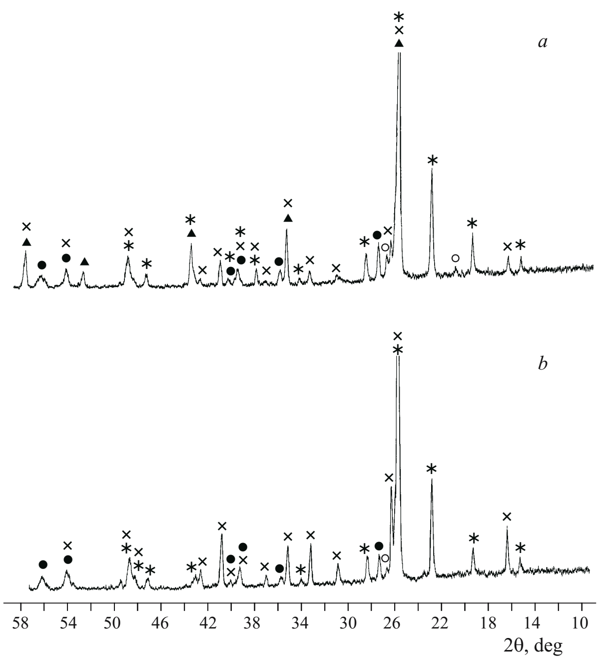

Fig. 1. Diffraction patterns of sample Si-7p (CuK_α radiation) fired at 1200°C (*a*) and 1300°C (*b*): ∗) β-spodumene; ○) α-SiO_2; ×) mullite; ●) rutile; ▼) α-Al_2O_3.

The phase composition of glasses produced by joint melting of the main components of spodumene glass and the catalyst had the same crystalline phases; however, mullite started to be formed already at 1100°C and its content grew with increasing temperature (Fig. 1). The only exception was glass with a Si catalyst as the additive. In this case mullite was crystallized in perceptible quantities at 1200°C. A comparison of the phase compositions and degrees of sintering of samples based on spodumene glass fired at different temperatures indicates that mullite plays an ambiguous role in this process (Table 1). On the one hand, it impedes active sintering of material at temperatures below 1300°C and, on the other hand, it expands the sintered state interval. This is clearly seen in the comparative analysis of samples of identical compositions synthesized by different methods.

As for boron oxide, it is preferable to introduce it in the course of melting into samples containing a TiO_2 catalyst. In this case the sintering temperature decreases by 50°C.

Table 2 shows the main properties of the most densely sintered samples based on β-spodumene.

It can be seen that the dielectric permeability of glass ceramics depends on the phase composition of samples. Samples Si-7, Si-7p, Si-9, and Si-9p have similar phase compositions and, accordingly, comparable dielectric parameters. However, even in this case the results depend on the quantitative content of the impurity phases (rutile and mullite). The quantity of rutile is higher in samples containing titanium dioxide and boron oxide catalysts, which increases their dielectric permeability. The increased values of this parameter in sample Si-6 are presumably due to the properties of the residual vitreous phase.

TABLE 1

Sample	Water absorption, %, at firing temperature, °C				
	1050	1100	1200	1300	1350
Si-6*	19.62	19.45	16.50	0.27	Is fused
Si-6p**	24.97	25.15	25.00	8.31	2.05
Si-7	23.68	23.20	18.60	1.20	Is fused
Si-7p	Is not sintered		26.60	4.25	1.04
Si-8	Is not sintered	19.80	19.00	Is fused	
Si-8p	The same	20.50	16.25	7.58	4.91
Si-9	23.30	22.46	17.40	1.60	Is fused
Si-9p	Is not sintered		9.00	0.80	The same

* Samples obtained by method 1.

** Samples obtained by method 2.

TABLE 2

Composition	Temperature, °C	Apparent density, g/cm³	Open porosity, %	Water absorption, %	Dielectric permeability	Dielectric loss tangent at frequency 1 kHz
Si-6	1350	2.395	0.60	0.27	13.80	0.024
Si-7	1300	2.430	3.30	1.20	8.89	0.008
Si-7p	1350	2.380	2.86	1.04	9.98	0.020
Si-9	1300	2.320	4.30	1.60	10.24	0.022
Si-9p	1300	2.390	2.22	0.80	10.98	0.020

The dielectric parameters were measured under frequencies varying from 0.3 to 30.0 Hz and the obtained materials were found to have steady dielectric characteristics (the increase in dielectric permeability is not higher than 2.0 – 2.5%).

It was found that in joint melting of all glass components, including the catalyst, the crystalline phases responsible for the properties of glass ceramics are formed at lower temperatures. For spodumene-based glass ceramics such a phase component is mullite, which expands the sintered state interval. With the joint introduction of titanium dioxide and boron oxide, the phase composition does not change, but the sintering process shifts to a lower-temperature range; the amount of rutile in this case grows.

At the same time it has been established that materials produced by different methods, but having an identical phase composition determined by their sintering temperature, have comparable properties. This suggests that the ceramic technology method can be used to produce glass ceramics based on β-spodumene with the desired dielectric parameters. In this case the opportunities for refining the composition and properties of spodumene-based materials are expanded compared with the glass technology traditionally used to produced glass ceramics.

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